Supplementary Material (ESI) for Green Chemistry

Carbonates: Eco-friendly Solvents for Palladium-Catalysed Direct Arylation of Heteroaromatics

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Spectroscopic data of the new products

2-(3-Formylphenyl)-benzoxazole (12)
^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ=10.06 (s, 1H), 8.62 (s, 1H), 8.38 (d, ^3J(H,H)=8.0 Hz, 1H), 7.90 (d, ^3J(H,H)=8.0 Hz, 1H), 7.75-7.65 (m, 1H), 7.56 (t, ^3J(H,H)=7.8 Hz, 1H), 7.50-7.45 (m, 1H), 7.40-7.20 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=191.3, 162.0, 150.8, 141.9, 137.0, 132.9, 131.6, 129.7, 129.2, 128.3, 125.7, 124.9, 120.3, 110.8. Elemental analysis: calcd (%) for $C_{14}H_9NO_2$ (223.23): C 75.33, H 4.06; found: C 75.31, H 4.02.

2-(2-Formylphenyl)-benzoxazole (15)
^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ=11.04 (s, 1H), 8.24 (d, ^3J(H,H)=8.0 Hz, 1H), 8.08 (d, ^3J(H,H)=8.0 Hz, 1H), 7.81 (m, 1H), 7.73 (t, ^3J(H,H)=7.8 Hz, 1H), 7.70-7.50 (m, 2H), 7.45-7.35 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=192.5, 160.5, 150.6, 141.9, 135.6, 133.6, 131.2, 129.8, 128.5, 128.4, 125.9, 124.9, 120.5, 110.7. Elemental analysis: calcd (%) for $C_{14}H_9NO_2$ (223.23): C 75.33, H 4.06; found: C 75.40, H 4.05.

2-(2-Trifluoromethylphenyl)-benzoxazole (17)
^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ=8.15 (d, ^3J(H,H)=8.0 Hz, 1H), 7.92-7.80 (m, 2H), 7.78-7.55 (m, 3H), 7.45-7.35 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=161.1, 151.1, 141.5, 132.1, 132.0, 131.8, 130.9, 129.2 (q, J=32.4 Hz), 127.0 (q, J=5.6 Hz), 125.6, 124.7, 123.6 (q, J=273.6 Hz), 120.5, 110.8. Elemental analysis: calcd (%) for $C_{14}H_8F_3NO$ (263.21): C 63.88, H 3.06; found: C 63.90, H 3.01.

4-Benzoxazol-2-ylisoquinoline (24)
^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ=9.44-9.31 (m, 3H), 8.00 (d, ^3J(H,H)=8.0 Hz, 1H), 7.90-7.82 (m, 2H), 7.66 (t, ^3J(H,H)=7.8 Hz, 1H), 7.62 (m, 1 H), 7.40-7.36 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=160.8, 155.4, 149.9, 145.0, 141.9, 132.5, 132.1, 128.3, 128.1, 127.7, 125.6, 125.4, 124.6, 120.2, 117.6, 110.5. Elemental analysis: calcd (%) for $C_{16}H_{10}N_2O$ (246.26): C 78.03, H 4.09; found: C 78.10, H 3.99.

Ethyl 2-(4-acetylphenyl)-oxazole-4-carboxylate (26)
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=8.31 (s, 1H), 8.19 (d, J(H,H)=8.5 Hz, 2H), 8.03 (d, J(H,H)=8.5 Hz, 2H), 4.42 (q, J(H,H)=7.2 Hz, 2H), 2.63 (s, 3H), 1.39 (t, J(H,H) = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=197.4, 161.5, 161.2, 144.4, 138.8, 135.2, 130.3, 128.9, 127.1, 61.6, 26.9, 14.4. Elemental analysis: calcd (%) for $C_{14}H_{13}NO_4$ (259.26): C 64.86, H 5.05; found: C 65.05, H 4.92.

5-(4-Cyanophenyl)-2-(4-methoxyphenyl)-oxazole-4-carboxylic acid ethyl ester (32)
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=8.24 (d, J(H,H)= 8.5 Hz, 2H), 8.03 (d, J(H,H)=8.7 Hz, 2H), 7.72 (d, J(H,H)=8.5 Hz, 2H), 6.95 (d, J(H,H)=8.7 Hz, 2H), 4.43 (q, J(H,H)=7.2 Hz, 2H), 3.83 (s, 3H), 1.41 (t, J(H,H)=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=162.2, 162.0, 160.7, 151.9, 132.1, 131.2, 130.2, 128.8, 128.63, 118.4, 114.3, 113.0, 61.8, 55.4, 14.2. Elemental analysis: calcd (%) for $C_{20}H_{16}N_2O_4$ (348.35): C 68.96, H 4.63; found: C 69.11, H 4.56.

2-(4-Cyano-phenyl)-5-(4-methoxy-phenyl)-oxazole-4-carboxylic acid ethyl ester (33)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=8.64 (d, J(H,H)=8.6 Hz, 2H), 8.23 (d, J(H,H)=8.1 Hz, 2H), 8.10 (d, J(H,H)=8.6 Hz, 2H), 7.76 (d, J(H,H)=8.1 Hz, 2H), 4.43 (q, J(H,H)=7.2 Hz, 2H), 3.87 (s, 3H), 1.41 (t, J(H,H)=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=162.0, 161.5, 156.7, 156.4, 150.6, 133.4, 130.4, 127.5, 120.2, 119.0, 114.0, 61.6, 55.4, 14.3. Elemental analysis: calcd (%) for $C_{20}H_{16}N_2O_4$ (348.35): C 68.96, H 4.63; found: C 69.06, H 4.85.

2-(4-Methoxyphenyl)-5-pyridin-4-yl-oxazole-4-carboxylic acid ethyl ester (34)
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=8.70 (d, J(H,H)=5.7 Hz, 2H), 8.04-7.98 (m, 4H), 6.93 (d, J(H,H)=9.0 Hz, 2H), 4.43 (q, J(H,H)=7.2 Hz, 2H), 3.80 (s, 3H), 1.39 (t, J(H,H)=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=162.3, 161.9, 160.9, 151.2, 150.2, 134.2, 130.9, 128.8, 121.5, 118.4, 61.8, 55.4, 14.2. Elemental analysis: calcd (%) for $C_{18}H_{16}N_2O_4$ (324.33): C 66.66, H 4.97; found: C 66.84, H 4.73.

3-(4-Methylthiazol-5-yl)-acetophenone (48)
^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ=8.70 (s, 1H), 8.01 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 2.62 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=197.9, 151.2, 149.6, 137.9, 134.1, 132.9, 131.2, 129.5, 129.4, 128.2. Elemental analysis: calcd (%) for $C_{12}H_{11}NOS$ (217.29): C 66.33, H 5.10; found: C 66.47, H 5.21.

3-(4-Methylthiazol-5-yl)-quinoline (49)
^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ=9.01 (s, 1H), 8.80 (s, 1H), 8.20 (s, 1H), 8.17 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=151.8, 150.9, 150.5, 147.7, 136.1, 130.5, 129.8, 128.7, 128.3, 127.8, 125.8, 16.6. Elemental analysis: calcd (%) for $C_{13}H_{10}N_2S$ (226.30): C 69.00, H 4.45; found: C 69.10, H 4.31.

***tert*-Butyl 5-phenylthiazole-4-carboxylate (50)**
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=8.75 (s, 1H), 7.46-7.40 (m, 5H), 1.39 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=161.3, 151.3, 144.9, 143.3, 130.9, 130.1, 129.1, 128.3, 82.2, 28.0. Elemental analysis: calcd (%) for $C_{14}H_{15}NO_2S$ (261.34): C 64.34, H 5.79; found: C 64.47, H 5.62.

***tert*-Butyl 5-(4-cyanophenyl)-2-phenyl-thiazole-4-carboxylate (51)**
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=8.00-7.97 (m, 2H), 7.72 (d, J(H,H)=8.4 Hz, 2H), 7.59 (d, J(H,H)=8.4 Hz, 2H), 7.48-7.43 (m, 3H), 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=167.1, 160.9, 144.2, 141.5, 136.2, 132.5, 131.9, 131.0, 130.8, 129.1, 126.9, 118.5, 112.6, 82.7, 27.9. Elemental analysis: calcd (%) for $C_{21}H_{18}N_2O_2S$ (362.44): C 69.59, H 5.01; found: C 69.58, H 5.05.

***tert*-Butyl 5-(4-methoxyphenyl)-2-phenyl-thiazole-4-carboxylate (52)**
^{1}H NMR ($CDCl_3$, 300 MHz) δ=8.00-7.97 (m, 2H), 7.45-7.39 (m, 5H), 6.94 (d, J(H,H)= 8.8 Hz, 2H), 3.85 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=165.4, 161.7, 160.3, 144.5, 143.0, 133.1, 131.3, 130.5, 129.0, 126.8, 123.3, 113.7, 82.0, 55.5, 28.0. Elemental analysis: calcd (%) for $C_{21}H_{21}NO_3S$ (367.46): C 68.64, H 5.76; found: C 68.56, H 5.72.